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EVALUATION OF A DIFFUSION/TRAPPING MODEL FOR HYDROGEN INGRESS IN HIGH-STRENGTH ALLOYS

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Hydrogen Ingress in Titanium[☆]

B. G. Pound^{*}

ABSTRACT

A potentiostatic pulse technique was used to study the ingress of hydrogen in titanium (pure and grade 2) in an acetate buffer. Hydrogen ingress did not occur with pure titanium, indicating that the surface oxide is an effective barrier to hydrogen entry. In contrast, the data for Ti grade 2 (UNS[†] R50400) were shown to fit a model for hydrogen diffusion and trapping, allowing values to be determined for the irreversible trapping constant (k) and the flux of hydrogen into the metal. Two values of k were obtained, depending on the level of hydrogen present in the metal. The density of irreversible traps calculated from k for low hydrogen levels suggests that the principal irreversible traps may be interstitial nitrogen, but grain boundaries are another possibility. The additional trapping constant obtained for high hydrogen levels is thought to be associated with hydride formation. The irreversible trapping constants for Ti grade 2 are consistent with its susceptibility to hydrogen embrittlement relative to that of other alloys. The results demonstrate that multiple irreversible traps can be distinguished by using the diffusion/trapping model.

KEY WORDS: hydrogen ingress, hydrogen diffusion, hydrogen trapping, potentiostatic, titanium

INTRODUCTION

Structural heterogeneities in alloys are potential trapping sites for diffusing hydrogen, and the interaction of hydrogen with these trap sites can render the alloy susceptible to hydrogen embrittlement. Hydrogen ingress in various iron- and nickel-base alloys has recently been studied using a potentiostatic pulse technique in which a test electrode is charged with hydrogen at a constant potential (E_c) for a time (t_c).¹⁻³ The potential is then stepped to a more positive value, E_a (10 mV negative of the open-circuit potential), and an anodic current transient is obtained. By using an appropriate diffusion/trapping model⁴ to analyze the data, it was possible to determine trapping parameters for these alloys. The technique and model have now been applied to titanium in both the pure and grade 2 forms to obtain the hydrogen ingress characteristics and then to compare the trapping capability of titanium with previously studied alloys in terms of their susceptibility to hydrogen embrittlement.

The diffusion/trapping model has been developed for two cases: (1) diffusion control, in which the rate of hydrogen ingress is controlled by diffusion in the bulk metal; and (2) interface control, in which the rate of ingress is controlled by the flux across the interface.⁴ For a film-covered metal or alloy, the interface control model has been found to be applicable in all cases so far. According to this model, the total charge passed out is given in nondimensional form by⁴

$$Q'(x) = \sqrt{R} [1 - e^{-R/\sqrt{\pi R}}] - [1 - 1/(2R) \operatorname{erf} \sqrt{R}] \quad (1)$$

The nondimensional terms are defined by $Q = q/[FJ\sqrt{(L/k_a)}]$ and $R = k_a L$ where q is the dimensionalized charge in $C \cdot m^{-2}$, F is the Faraday constant, and J is the ingress flux in $mol \cdot m^{-2} \cdot s^{-1}$. The charge $q'(x)$ corresponding to $Q'(x)$ is equated to the charge (q_a) associated with the experimental anodic transients. k_a is an apparent trapping constant measured for irreversible traps in the presence of reversible traps and can be expressed by $k(D_a/D_L)$ where k is the irreversible trapping constant, D_a is the apparent diffusivity, and D_L is the lattice diffusivity of hydrogen in the metal.

Data for the anodic charge (q_a) were obtained by integration of the current transients for different charging times and were fitted to Equation (1) to determine k_a and J . Values of these two parameters can be used to calculate the charge (q_T) irreversibly trapped given nondimensionally by

$$Q_T = [\sqrt{R} - 1/(2\sqrt{R})] \operatorname{erf} \sqrt{R} + e^{-R/\sqrt{\pi R}} \quad (2)$$

The charge associated with the entry of hydrogen into the metal (q_m) can be determined from its nondimensional form of $Q_m = \sqrt{R}$ by using the derived value of k_a . The data for q_m , q_T , and the cathodic charge (q_c) can then be used to obtain two ratios:

(1) q_T/q_m , corresponding to the fraction of hydrogen in the metal that is trapped; and (2) q_m/q_c , representing the fraction of charge associated with hydrogen entry during the charging step. The ratio q_T/q_m is independent of potential because each component has the same dependence on flux, whereas q_m/q_c generally exhibits some variation with potential.

The density of irreversible trap particles (N_t) can be obtained directly from the apparent trapping constant (k_a) by using a model⁵ based on spherical traps of radius d :

$$N_t = k_a a / (4\pi d^2 D_a) \quad (3)$$

where a is the diameter of the metal atom. The calculation of N_t requires a value for d , and therefore a knowledge of potential irreversible traps in terms of the dimensions of heterogeneities in the

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[†]UNS numbers are listed in Metals and Alloys in the Unified Numbering System, published by the Society of Automotive Engineers (SAE) and cosponsored by the American Society for Testing and Materials (ASTM).

alloy of interest. The dominant irreversible trap can then be identified by comparing the trap density with the concentrations of potential traps in the alloy.

EXPERIMENTAL PROCEDURE

The composition of Ti grade 2 provided by the manufacturer was as follows: 0.021 C, 0.17 Fe, 0.007 N, 0.16 O, <0.0050 H, with the balance being Ti. The titanium specimen was 99.99 percent pure. Both grades of titanium were supplied in the form of 12.7-mm diameter rods and were used in the as-received condition. The yield strength of the as-received Ti grade 2 was given as 380 MPa.

Details of the electrochemical cell and instrumentation have been given previously.² The test electrodes consisted of a 5-cm length of rod in a polytetrafluoroethylene sheath so that only the planar end surface was exposed to the electrolyte. The surface was polished with SiC paper followed by 0.05- μ m alumina powder before each test to remove metal previously exposed to adsorbed hydrogen. The electrolyte was an acetate buffer containing 1 M acetic acid and 1 M sodium acetate with 15 ppm As_2O_3 . The electrolyte was deaerated with argon for 1 hour before measurements began and throughout data acquisition. The potentials were measured with respect to a saturated calomel electrode (SCE). All tests were performed at $22 \pm 2^\circ C$.

The test electrode was charged with hydrogen for charging times from 0.5 to 50 s for each E_c . Anodic current transients were obtained for each charging time over a range of overpotentials ($\eta = E_c - E_{oc}$). The open-circuit potential (E_{oc}) of the test electrode was sampled immediately before each charging time and was also used to monitor the stability of the surface film.

RESULTS

Pure Titanium

A typical anodic current transient is shown in Figure 1. The anodic charge was invariant with t_c , which is not predicted by the diffusion/trapping model for either diffusion or interface control. Therefore, k_a could not be determined at any overpotential over the wide range studied (-0.05 to -0.8 V). The open-circuit potential, and therefore the charging potential, generally exhibited a positive shift over the range of charging times for each overpotential. This shift might compensate for the increase in t_c . However, in several cases, E_c changed by ≤ 5 mV and q_a was essentially constant. Therefore, any effect resulting from the shift in E_c appears to be minor. Instead, the invariance in q_a indicates that negligible hydrogen enters the metal, so that q_a is approximately zero, and therefore q_a corresponds solely to oxidation of the adsorbed layer of hydrogen; that is, it should comprise only q_{ads} . The dependence of $\log q_a$ on η (Figure 2) is linear over a wide potential range, as expected if $q_a \sim q_{ads}$. The lack of dependence at high overpotentials probably corresponds to full coverage of the adsorbed hydrogen layer.

Titanium Grade 2

An anodic current transient for Ti grade 2 is shown in Figure 3. The grade 2 metal, in contrast to the pure form, exhibits a marked dependence of q_a on t_c , so trapping constants can be evaluated in this case. The anodic charge essentially involved adsorbed hydrogen. Data for q_a could be analyzed in terms of the interface control model using Equation (1) to obtain values of k_a and J that were independent of charging potential (E_c) and charging time (t_c), respectively. In accordance with previous practice,² the data were analyzed only for charging times ≥ 10 s to minimize short-time effects where, for example, oxidation of the adsorbed hydrogen layer can make a significant contribution to q_a . Four tests were performed, and the values of k_a and J given in Table 1

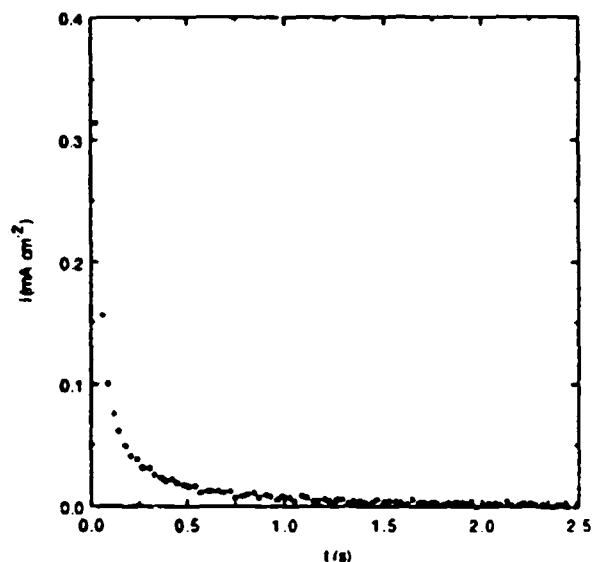


FIGURE 1. Anodic transient for pure titanium in acetate buffer. $t_c = 15$ s; $E_c = -0.887 V_{SCE}$. The full transient is not shown.

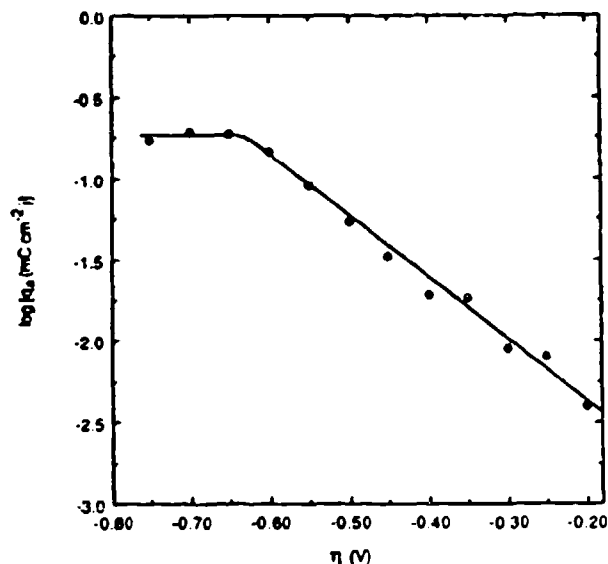


FIGURE 2. Dependence of anodic charge on overpotential for pure titanium in acetate buffer.

for two of the tests are typical of the overall results. The flux increases with overpotential as a result of the dependence of J on the surface coverage of H_{ads} . The variation in $\log J$ with η shown in Figure 4 is linear, as is required with the assumption that the surface coverage respond rapidly to changes in potential.

In both tests, k_a is independent of overpotential but exhibits two values depending on the potential range. At charging potentials up to approximately -0.93 V, k_a is $0.028 \pm 0.002 s^{-1}$, whereas the mean value at higher potentials is $0.040 s^{-1}$. The two other tests gave trapping constants of $0.036 s^{-1}$ and $0.042 s^{-1}$ at high potentials, so that the mean value of k_a at high potentials in the four tests was $0.040 \pm 0.004 s^{-1}$. Values of q_a calculated using k_a and J are compared with the corresponding experimental data ($\eta = -0.70$ V in test 2) in Figure 5, and it is evident that the data agree well over the charging time range.

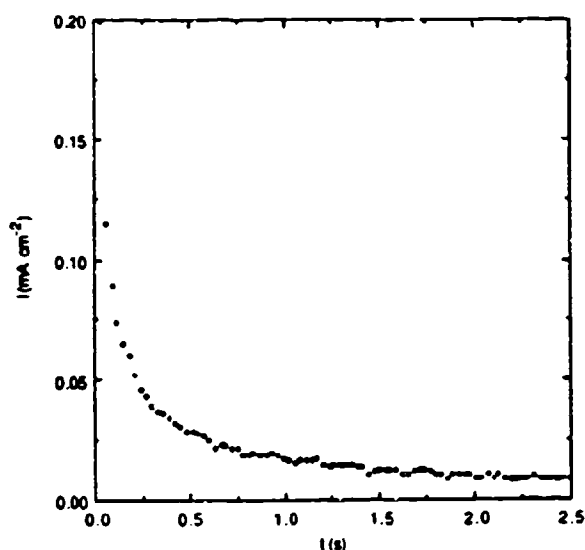


FIGURE 3. Anodic transient for Ti grade 2 in acetate buffer. $t_c = 15$ s; $E_c = -0.742$ V_{SCE}. The full transient is not shown.

TABLE 1
Values of k_a and J for Titanium Grade 2

| Test | η (V) | E_c (V _{SCE}) | k_a (s ⁻¹) | J (nmol·cm ⁻² ·s ⁻¹) | Mean k_a |
|------|---------------|------------------------------|-----------------------------|--|-------------------|
| 1 | -0.55 | -0.614 | 0.029 | 0.07 | 0.028 ± 0.002 |
| | -0.60 | -0.652 | 0.034 | 0.08 | |
| | -0.65 | -0.708 | 0.025 | 0.08 | |
| | -0.70 | -0.751 | 0.024 | 0.09 | |
| | -0.75 | -0.806 | 0.028 | 0.13 | |
| | -0.80 | -0.868 | 0.029 | 0.17 | |
| | -0.85 | -0.930 | 0.029 | 0.22 | 0.044 ± 0.002 |
| | -0.90 | -1.040 | 0.044 | 0.39 | |
| | -0.95 | -1.062 | 0.044 | 0.44 | |
| | -1.00 | -1.137 | 0.049 | 0.56 | |
| | -1.05 | -1.203 | 0.042 | 0.59 | |
| | -1.10 | -1.283 | 0.044 | 0.69 | |
| 2 | -1.15 | -1.370 | 0.041 | 0.73 | 0.028 ± 0.001 |
| | -0.60 | -0.655 | 0.031 | 0.07 | |
| | -0.65 | -0.692 | 0.028 | 0.08 | |
| | -0.70 | -0.741 | 0.029 | 0.09 | |
| | -0.75 | -0.796 | 0.027 | 0.11 | |
| | -0.80 | -0.857 | 0.027 | 0.14 | |
| | -0.85 | -0.921 | 0.028 | 0.19 | 0.036 ± 0.003 |
| | -0.90 | -0.987 | 0.034 | 0.29 | |
| | -0.95 | -1.024 | 0.033 | 0.30 | |
| | -1.00 | -1.111 | 0.039 | 0.40 | |
| | -1.05 | -1.182 | 0.041 | 0.49 | |
| | -1.10 | -1.258 | 0.035 | 0.49 | |
| | -1.15 | -1.310 | 0.034 | 0.51 | |

The increase in trapping constant at high overpotentials can be ascribed to an additional type of irreversible trap participating concurrently with the irreversible traps detected at low overpotentials. The densities of the two traps are assumed to be additive, and therefore k_a at high overpotentials can be represented by

$$k_a = k_{a1} + k_{a2} \quad (4)$$

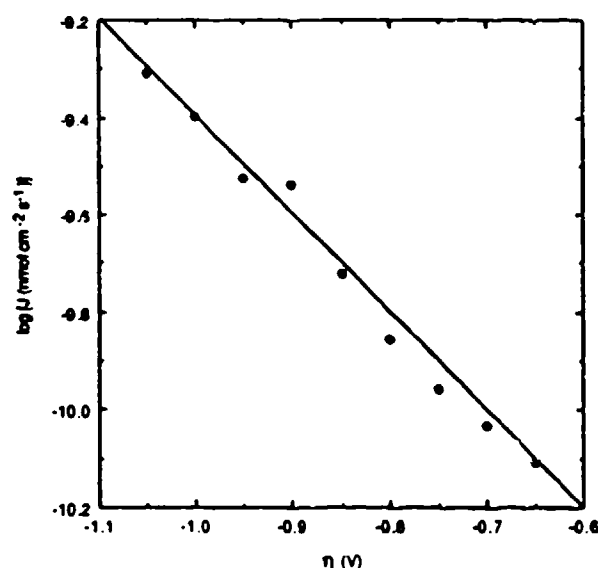


FIGURE 4. Dependence of flux on overpotential for Ti grade 2.

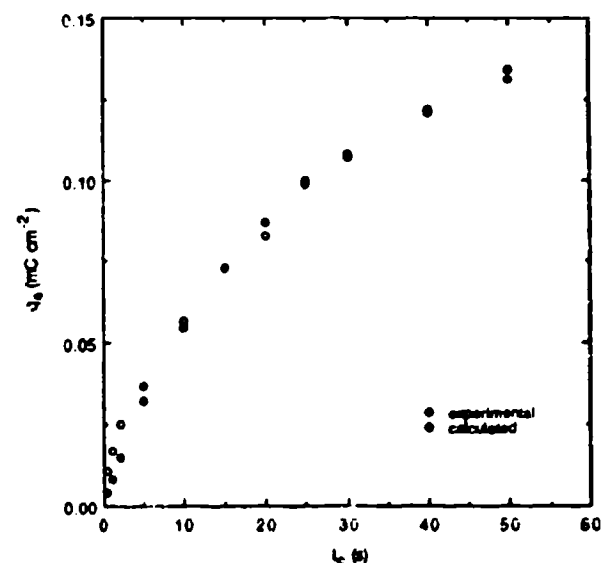


FIGURE 5. Comparison of experimental and calculated anodic charge data for Ti grade 2 in acetate buffer. $E_c = -0.742$ V.

where k_{a1} corresponds to the irreversible traps detected at low η and k_{a2} is associated with the additional type of trap. The total trapping constant (k_a) was taken as the mean (0.040 s⁻¹) of the high η results, and $k_{a1} = 0.028 \pm 0.002$ s⁻¹, so $k_{a2} = 0.012 \pm 0.006$ s⁻¹.

Data for the charge ratios as a function of t_c at low overpotentials are shown in Figures 6 and 7. The q_T/q_m ratio for Ti grade 2 approximately follows an empirical $\sqrt{t_c}$ dependence for charging times up to 10 s, but shows an increasing deviation from linearity at higher charging times, which can be attributed to the different dependence of q_T and q_m on t_c .

The ratio of q_m to q_c increases with t_c , and the increase becomes greater at higher overpotentials (Figure 8). The increase in q_m/q_c with overpotential indicates that hydrogen entry becomes more efficient, which in turn implies that hydrogen atom recombination during charging on Ti grade 2 must occur electrochemically. If chemical recombination were involved, its rate ($\propto \theta^2$ where θ is

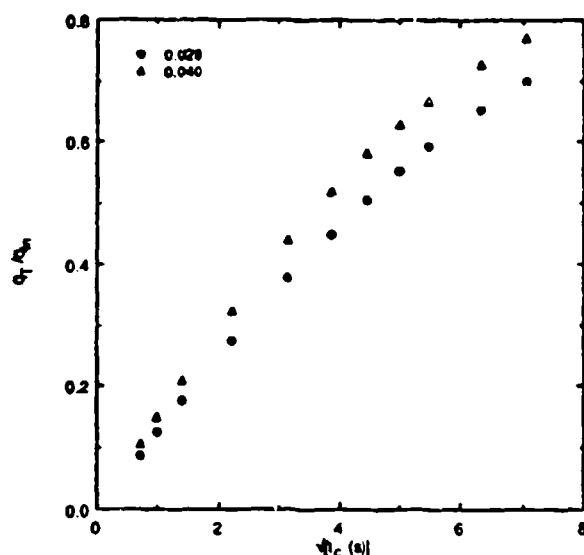


FIGURE 6. Dependence of q_r/q_m on charging time for Ti grade 2 with $k_s = 0.028 \text{ s}^{-1}$ and 0.040 s^{-1} .

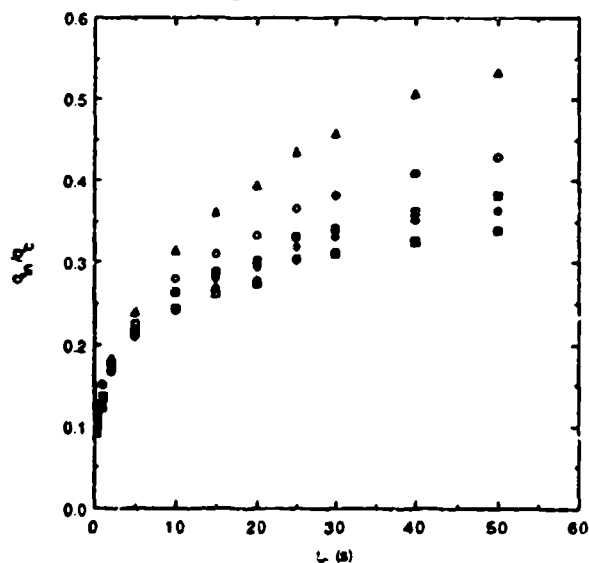


FIGURE 7. Dependence of q_r/q_c on charging time for Ti grade 2 at low overpotentials: \square -0.60 V; \bullet -0.65 V; \diamond -0.70 V; \blacksquare -0.75 V; \circ -0.80 V; \triangle -0.85 V.

the surface coverage) should increase relative to the rate of hydrogen entry ($\propto \theta$) at high overpotentials, resulting in a loss of charging efficiency. A similar conclusion was reached in studies⁵ of titanium in sulfuric acid solutions between pH 0.25 and 2.25; under these conditions, hydrogen evolution is believed to occur on an oxide film at potentials more positive than approximately -1.0 V_{ec} and to involve electrochemical desorption as the rate-determining step.

The data for q_r/q_m at high overpotentials exhibits nonlinear behavior similar to that for this ratio at low overpotentials (Figure 6). In addition, q_r/q_c in general increases with t_c , as shown in Figure 9, but varies with η in the opposite manner from that found for low overpotentials; that is, q_r/q_c is high at the low end of the overpotential range and decreases as η increases (Figure 10). This reduction in the efficiency of hydrogen entry can be explained by the formation of a hydride, as discussed later.

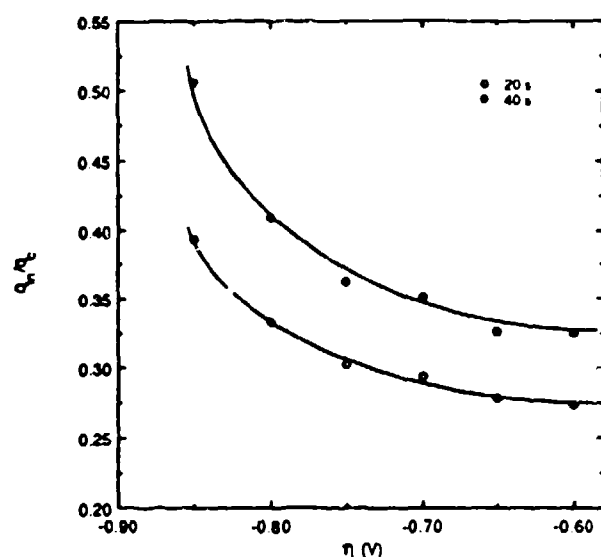


FIGURE 8. Dependence of q_r/q_c on overpotential for Ti grade 2 at low overpotentials and charging times of 20 s and 40 s.

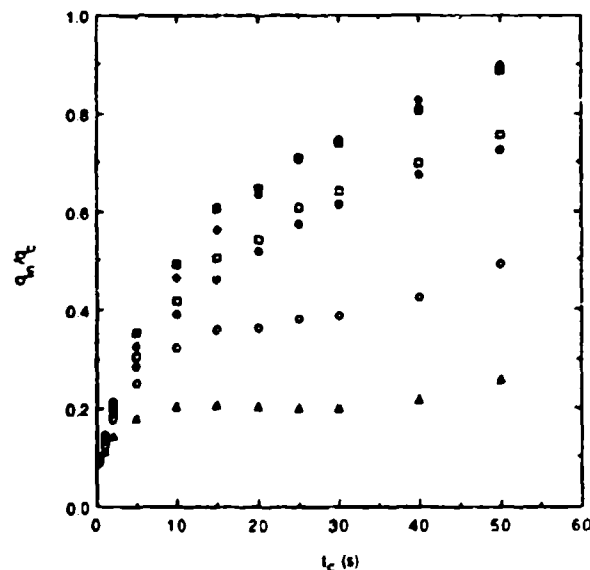


FIGURE 9. Dependence of q_r/q_c on charging time for Ti grade 2 at high overpotentials: \square -0.90 V; \bullet -0.95 V; \diamond -1.00 V; \blacksquare -1.05 V; \circ -1.10 V; \triangle -1.15 V.

DISCUSSION

Pure Titanium

Titanium in the pure form appears to be resistant to hydrogen penetration. The surface film formed on pure titanium in aqueous solutions is known to be a highly effective barrier to hydrogen entry. Thus, the anodic charge data are consistent with the presence of a hydrogen barrier. Previous work on single crystal TiO_2 in the rutile form⁶ has shown that the diffusivity of hydrogen at 20°C is about four orders of magnitude higher for the c-axis ($1.9 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$) than for the a-axis ($7.5 \times 10^{-20} \text{ m}^2 \text{ s}^{-1}$). The orientation of the film was not investigated in this work, but it clearly can determine the resistance of titanium to hydrogen entry and may account for the difference in charging behavior of the pure and grade 2 forms of titanium.

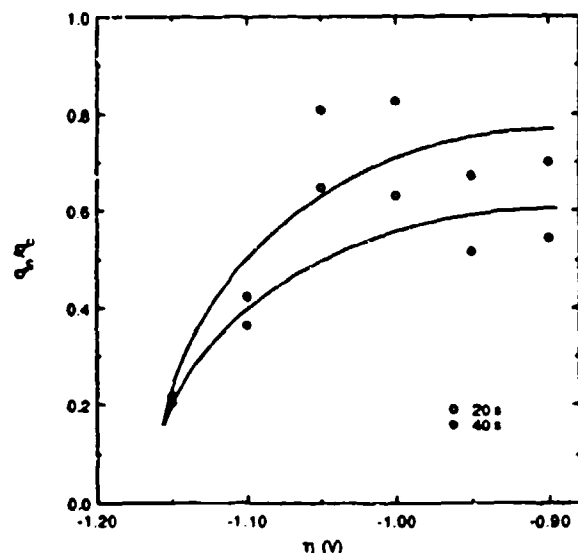


FIGURE 10. Dependence of q_{∞}/q_c on overpotential for Ti grade 2 at high overpotentials and charging times of 20 and 40 s.

Titanium Grade 2

The irreversible trapping constants (k_1 and k_2) for Ti grade 2 can be approximated to the apparent trapping constants on the basis of the low diffusivity of hydrogen in titanium and the closeness in the composition of grade 2 and pure titanium. The diffusivity of hydrogen in α -Ti over the temperature range 25 to 100°C is expressed by

$$D = 6 \times 10^{-6} \exp \left[\frac{(-60250 \pm 3350 \text{ J mol}^{-1})}{RT} \right] \text{ m}^2 \text{ s}^{-1} \quad (5)$$

which gives a value of $1.65 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$ at 25°C.⁷ Because of the diffusivity and composition factors, the diffusivities for the pure and commercial grades are assumed to differ negligibly, so that $D_s \sim D_c$, and therefore $k \sim k_s$. Hence, $k_1 = 0.028 \pm 0.002 \text{ s}^{-1}$ and $k_2 = 0.012 \pm 0.006 \text{ s}^{-1}$.

The trapping at low overpotentials as reflected by the value of 0.028 s^{-1} for k_1 could be associated with either the minor elements (C, N, O, and Fe) or structural defects such as grain boundaries and dislocations in the titanium. Equation (3) was used to calculate the density of irreversible traps from k_1 , by assuming that the principal type of trap was one of the minor elements. The appropriate atomic radius was therefore used as the trap radius (d) and the diameter (a) of the titanium atom was taken as 290 pm. The values of N_i and the atomic concentration (A) of the elements are given in Table 2. The ratio A/N_i represents the level of agreement between the atomic concentration and the trap density calculated on the basis of the appropriate element.

In all cases except nitrogen, A/N_i is large enough to discount these elements as the principal irreversible trap, even allowing for the uncertainty in the hydrogen diffusivity, which could vary N_i by a factor of almost four. Moreover, oxygen is known to reduce the solubility of hydrogen in titanium,⁸ which suggests that oxygen is unlikely to be a potential trap; this is consistent with the above results. However, a reasonable correlation exists for nitrogen, particularly because the uncertainty factor means that the calculated trap density may be no more than five times larger than the actual concentration of nitrogen atoms. Interestingly, among the interstitials, nitrogen is particularly effective in reducing the ductility of titanium,⁹ which coincides with its apparent role as the principal irreversible trap. Hence, nitrogen may strongly affect the susceptibility of Ti grade 2 to hydrogen embrittlement through its combined influence on brittleness and hydrogen trapping.

TABLE 2
Values of N_i for Titanium Grade 2

| Element | d (pm) | N_i (m^{-3}) | A (m^{-3}) | A/N_i |
|---------|-------------|------------------------------|----------------------------|---------|
| C | 77 | 6.8×10^{23} | 4.8×10^{25} | 71 |
| N | 74 | 7.4×10^{23} | 1.4×10^{25} | 19 |
| O | 74 | 7.4×10^{23} | 2.7×10^{26} | 365 |
| Fe | 124 | 2.6×10^{23} | 8.3×10^{25} | 316 |

Although the data suggest that the principal irreversible trap may be nitrogen, grain boundaries are another possibility; however, in the case of steels, the trapping energy of grain boundaries, and therefore their reversible/irreversible nature, depends on their angular orientation.⁹ A more likely alternative is that trapping results from hydride formation. Hydride decomposition is expected to be slow relative to the duration of a pulse test, and hence the hydrogen can be considered irreversibly trapped.

Previous work by Satoh et al. showed that unalloyed titanium absorbs hydrogen in near-neutral brine at 25 and 100°C when the potential is more negative than $-0.75 V_{\text{SCE}}$.¹⁰ These workers found that only thin surface hydride films form at potentials more positive than $-1.0 V_{\text{SCE}}$, but extensive hydride formation may occur at more negative potentials. Traps corresponding to the formation of a surface hydride could be expected to saturate at potentials approaching the commencement of accelerated hydride formation because of the decreasing availability of free titanium in the vicinity of the surface. Trap saturation would lead to a decrease in k_1 with increasing overpotential, but such a decrease is not observed. Therefore, it seems more likely that nitrogen, rather than surface hydride formation or grain boundaries, acts as the principal trap at low overpotentials. The additional trapping constant (k_2) obtained at high overpotentials ($E_c < -0.93 V_{\text{SCE}}$) is probably associated with the accelerated formation of hydrides. Moreover, the decrease in q_{∞}/q_c in this potential region is consistent with the presence of a partial barrier to hydrogen entry and provides support for the formation of a thick hydride layer.

Comparison of Trapping Constants

The irreversible trapping constants for Ti grade 2 are compared with those obtained previously² for a range of alloys shown in Table 3. Although various metallurgical factors are involved, the susceptibility to hydrogen embrittlement does appear to follow the trapping capability of the alloy as represented by the irreversible trapping constant. This correlation has been discussed earlier for the steels and nickel-base alloys listed.³

From the order of the trapping constants, the susceptibility of Ti grade 2 to hydrogen embrittlement at low levels of hydrogen is predicted to be comparable to that of Incoloy⁽²⁾ 925 (UNS N09925) and MP35N (UNS R30035). Hydride precipitates can be observed in Ti grade 2 at hydrogen concentrations above ~100 ppm by weight, but they do not cause gross embrittlement of the titanium until hydrogen levels exceed 500 to 600 ppm.¹¹ Similarly, gas-phase charging studies of Incoloy 903 have shown that prolonged exposure is required to accumulate enough hydrogen to reduce ductility.¹² Incoloy 925 is likely to behave similarly to the 903 grade, so the trapping constant for Ti grade 2 is consistent with that of Incoloy 925 in terms of hydrogen embrittlement resistance in that relatively long exposure times are required in each case for the hydrogen concentration to exceed the level necessary to degrade the mechanical properties. Furthermore, the higher trapping constant (0.040 s^{-1}) associated with the occurrence of significant hydride formation coincides with the increasing susceptibility to embrittlement with hydrogen concentration.

⁽²⁾Incoloy is a trade name of Inco Alloys International Inc., Huntington, WV.

TABLE 3
Irreversible Trapping Constants

| Alloy | k (s ⁻¹) |
|---------------------------|-------------------------|
| 4340 steel | 4.0 ± 0.5 |
| 18Ni (300) maraging steel | 1.50 ± 1.05 |
| Inconel 718 | 0.128 ± 0.024 |
| Monel K-500 | 0.040 ± 0.010 |
| Ti grade 2 (high H) | 0.040 ± 0.008 |
| Incoloy 925 | 0.034 ± 0.004 |
| Ti grade 2 (low H) | 0.028 ± 0.002 |
| MP35N | 0.026 ± 0.002 |

SUMMARY

► The ingress of hydrogen in Ti grade 2 was shown to fit a diffusion/trapping model under interface control. Pure titanium does not absorb hydrogen because of the effectiveness of the surface oxide as a barrier to entry.

► In the case of Ti grade 2, interstitial nitrogen appears to be the principal irreversible trap at low hydrogen levels, although grain boundaries are another possibility. When the concentration of hydrogen becomes high enough, hydride formation provides an additional form of trapping.

► The irreversible trapping constants for Ti grade 2 are consistent with its relative susceptibility to hydrogen embrittlement. From the order of the trapping constants, Ti grade 2 at low levels of hydrogen is predicted to be comparable to Incoloy 925 and MP35N in terms of hydrogen embrittlement resistance.

► The presence of multiple irreversible traps involving interstitial elements (or grain boundaries) and hydride formation can be distinguished by using the diffusion/trapping model.

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